

533 Rec'd PCT/PTO 11 AUG 2000

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#3

PATENT

Attorney Docket No. 5725.0632-00



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re National Phase )  
Application of PCT/FR98/02831: )  
Gérard LANG et al. ) Group: Not Yet Assigned  
Serial No.: 09/600,128 ✓ ) Examiner: Not Yet Assigned  
PCT Filed: December 22, 1998 )  
National Stage Entry: July 12, 2000 )

For: KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING  
LACCASE AND DYEING METHOD USING SAME

Assistant Commissioner for Patents  
Washington, D.C. 20231

TRANSMITTAL LETTER

Sir:

Enclosed is a Preliminary Amendment for the above identified application.

The claims are calculated below:

	Claims Remaining After Amendment		Highest Number Previously Paid	Present Extra	Rate	Additional Fee
Total	34	-	30	4	x \$ 18	\$72.00
Indep.	4	-	3	1	x \$ 78	\$78.00
[ ] First Presentation of Multiple Dep. Claim(s)					+\$260	
Subtotal						\$150.00
Reduction by 1/2 if small entity						-
TOTAL						\$150.00

A check for \$150.00 to cover the cost of the additional claims added by this Preliminary  
Amendment is enclosed.

08/15/2000 ERIMANDO 00000046 09600128

01 FC:966  
02 FC:964

72.00 DP  
78.00 DP

LAW OFFICES  
FINNEGAN, HENDERSON,  
FARABOW, GARRETT,  
& DUNNER, L.L.P.  
1300 I STREET, N.W.  
WASHINGTON, DC 20005  
202-408-4000

TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

International Application. No.

PCT/FR98/02831

International Filing Date

December 22, 1998

Priority Date Claimed

January 13, 1998

**Title of Invention: KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING A LACCASE AND DYEING METHOD USING SAME**

**Applicant(s) For DO/EO/US: Gérard LANG, and Jean COTTERET**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [x] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [x] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. [ ] is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. [x] has been transmitted by the International Bureau.
  - c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [x] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [x] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. [ ] have been transmitted by the International Bureau.
  - c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
  - d. [x] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11. to 16. below concern other document(s) or information included:**

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [ ] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
16. [ ] Other items or information:
  - a. [ ] Verified Small Entity Statement.
  - b. [ ] Copy of Notification of Missing Requirements.

09/600128

PCT/FR98/02831

05725,0632

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12 JUL 2000

17. [X] The following fees are submitted:

CALCULATIONS

**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO.....\$840.00

International preliminary examination fee paid to

USPTO (37 CFR 1.482).....\$670.00

No international preliminary examination fee paid to

USPTO (37 CFR 1.482) but international search fee

paid to USPTO (37 CFR 1.445(a)(2)).....\$690.00

Neither international preliminary examination fee

(37 CFR 1.482) nor international search fee

(37 CFR 1.445(a)(2)) paid to USPTO.....\$970.00

International preliminary examination fee paid to USPTO

(37 CFR 1.482) and all claims satisfied provisions

of PCT Article 33(1)-(4).....\$ 96.00

**ENTER APPROPRIATE BASIC FEE AMOUNT = \$840.00**

Surcharge of \$130.00 for furnishing the oath or declaration later than

[ ] 20 [ ] 30 months from the earliest claimed priority date

(37 CFR 1.492(e)).

\$

Claims	Number Filed	Number Extra	Rate	
Total Claims	33-20=	13	X \$18.00	\$234.00
Independent Claims	1- 3=		X \$78.00	\$
Multiple dependent claim(s) (if applicable)			+\$260.00	\$260.00

**TOTAL OF ABOVE CALCULATIONS = \$1334.00**

Reduction by 1/2 for filing by small entity, if applicable. Verified

Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28)

\$

**SUBTOTAL = \$1334.00**

Processing fee of \$130.00 for furnishing the English translation later

than [ ] 20 [ ] 30 months from the earliest claimed priority date

(37 CFR 1.492(f)).

\$

+

**TOTAL NATIONAL FEE = \$1334.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The

assignment must be accompanied by an appropriate cover sheet

(37 CFR 3.28, 3.31).

\$40.00 per property + \$

**TOTAL FEES ENCLOSED = \$1334.00**

Amount to be

refunded \$

charged \$

a. [X] A check in the amount of \$ 1334.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. \_\_\_\_\_ in the amount of


\$

to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 06-0916. A duplicate copy of this sheet is enclosed.

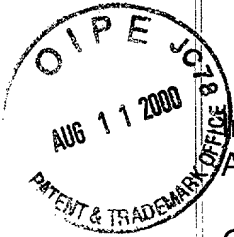
The Commissioner is hereby authorized to charge any other fees due under 37 C.F.R. \$1.16 or \$1.17 during the pendency of this application to our Deposit Account No. 06-0916.

SEND ALL CORRESPONDENCE TO:  
 Finnegan, Henderson, Farabow  
 Garrett & Dunner, L.L.P.  
 1300 I Street, N.W.  
 Washington, D.C. 20005-3315  
 EFC/FPD/dvz

  
 Ernest F. Chapman  
 Reg. No. 25,961

Submitted: July 12, 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



International Phase )  
Application of PCT/FR98/02831: )  
Gérard LANG et al. ) Group: Not Yet Assigned  
Serial No.: 09/600,128 ) Examiner: Not Yet Assigned  
PCT Filed: December 22, 1998 )  
National Stage Entry: July 12, 2000 ) **BOX PCT**

For: KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING  
LACCASE AND DYEING METHOD USING SAME

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

**PRELIMINARY AMENDMENT**

Prior to the examination of the above-referenced application on the merits,  
please amend the application as follows:

**IN THE CLAIMS:**

Please cancel claims 1-31 without prejudice or disclaimer to the subject matter  
contained therein.

Please add new claims 32-65 as follows:

- 32. A composition for the oxidation dyeing of keratin fibers, comprising:
- (a) at least one oxidation dye chosen from heterocyclic oxidation bases,  
heterocyclic couplers, and acid addition salts of said oxidation dyes; and
  - (b) at least one laccase-type enzyme,

provided that said heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy-pyrimidine and 3,4-diaminohydroxy-pyrazole, and

provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds.

33. The composition according to Claim 32, wherein said keratin fibers are human keratin fibers.

34. The composition according to Claim 33, wherein said human keratin fibers are hair.

35. The composition according to Claim 32, wherein said at least one enzyme of the laccase type is chosen from laccases of plant origin, animal origin, fungal origin and bacterial origin, and laccases obtained by biotechnology.

36. The composition according to claim 32, wherein said at least one enzyme of the laccase type is of plant origin and is chosen from the laccases extracted from plants chosen from Anacardiaceae, Podocarpaceae, Rosmarinus off., Solanum tuberosum, Iris sp., Coffea sp., Daucus carota, Vinca minor, Persea americana, Catharethus roseus, Musa sp., Malus pumila, Ginkgo biloba, Monotropa hypopithys, Aesculus sp., Acer pseudoplatanus, Prunus persica, and Pistacia palaestina.

37. The composition according to Claim 32, wherein said at least one enzyme of the laccase type is of microbial origin or obtained by biotechnology.

38. The composition according to Claim 32, wherein said at least one enzyme of the laccase type is chosen from the laccases obtained from fungi chosen from

DOCKET# 8270960

Polyporus versicolor, Rhizoctonia praticola, Rhus vernicifera, Scytalidium, Polyporus pinsitus, Myceliophthora thermophila, Rhizoctonia solani, Pyricularia orizae, Trametes versicolor, Fomes fomentarius, Chaetomium thermophile, Neurospora crassa, Colorius versicol, Botrytis cinerea, Rigidoporus lignosus, Phellinus noxius, Pleurotus ostreatus, Aspergillus nidulans, Podospora anserina, Agaricus bisporus, Ganoderma lucidum, Glomerella cingulata, Lactarius piperatus, Russula delica, Heterobasidion annosum, Thelephora terrestris, Cladosporium cladosporioides, Cerrena unicolor, Coriolus hirsutus, Ceriporiopsis subvermispora, Coprinus cinereus, Panaeolus papilionaceus, Panaeolus sphinctrinus, Schizophyllum commune, Dichomitius squalens, and variants of all said fungi.

39. The composition according to claim 32, wherein said at least one enzyme of the laccase type is in an amount ranging from 0.5 Lacu to 200 Lacu units per 100 g of said composition.

40. The composition according to claim 32, wherein said heterocyclic oxidation bases are chosen from pyrimidine derivatives, pyrazole derivatives, and acid addition salts of said heterocyclic oxidation bases.

41. The composition according to Claim 40, wherein said pyrimidine derivatives are chosen from 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, pyrazolopyrimidine derivatives, and acid addition salts of said pyrimidine derivatives.

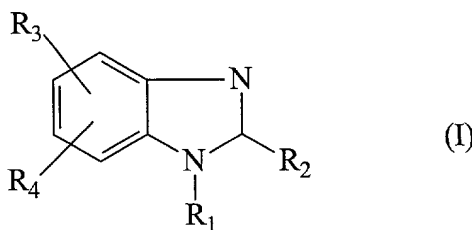
42. The composition according to Claim 41, wherein said pyrazolpyrimidine derivatives are chosen from pyrazolo pyrimidine-3,7-diamine, 2-methylpyrazolo pyrimidine-3,7-diamine, 2,5-dimethyl pyrazolo pyrimidine-3,7-diamine, pyrazolo pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo pyrimidine-3,5-diamine, 3-aminopyrazolo pyrimidin-7-ol, 3-amino-5-methylpyrazolo pyrimidin-7-ol, 3-amino-pyrazolo pyrimidin-5-ol, 2-(3-aminopyrazolo-pyrimidin-7-ylamino)ethanol, 3-amino-7- $\beta$ -hydroxyethylamino-5-methylpyrazolo pyrimidine, 2-(7-aminopyrazolo pyrimidin-3-ylamino)ethanol, 2-ethanol, 2-ethanol, 5,6-dimethylpyrazolo pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo pyrimidine-3,7-diamine, and 2,5,N7,N7-tetramethylpyrazolo pyrimidine-3,7-diamine, and acid addition salts of said pyrazolpyrimidine derivatives and tautomeric forms of said pyrazolpyrimidine derivatives, when a tautomeric equilibrium exists.

43. The composition according to Claim 40, wherein said pyrazole derivatives are chosen from 4,5-diaminopyrazole, 4,5-diamino-1-methyl-pyrazole, 1-benzyl-4,5-diaminopyrazole, 3,4-diamino-pyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-pyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4-methoxyphenyl) pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,

4,5-diamino-3-methyl-1-isopropylpyrazole, and acid addition salts of said pyrazole derivatives.

44. The composition according to claim 32, wherein said heterocyclic couplers are chosen from benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives, pyrazoloazole derivatives, pyrroloazole derivatives, imidazoloazole derivatives, pyrazolopyrimidine derivatives, pyrazoline-3,5-dione derivatives, pyrrolo-oxazoline derivatives, pyrazolo-thiazole derivatives, thiazoloazole S-oxide derivatives, thiazoloazole S,S-dioxide derivatives, and acid addition salts of said heterocyclic couplers.

45. The composition according to Claim 44, wherein said benzimidazole derivatives are chosen from the compounds of formula (I), and their acid addition salts:



in which:

- R<sub>1</sub> is chosen from hydrogen and C<sub>1</sub>-C<sub>4</sub> alkyl groups,
- R<sub>2</sub> is chosen from hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl groups, and phenyl groups,
- R<sub>3</sub> is chosen from hydroxyl groups, amino groups, and methoxy groups,



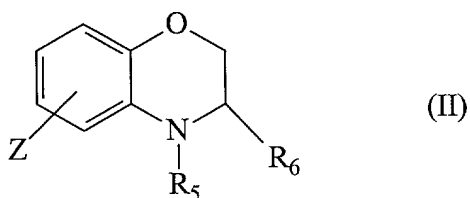
-R<sub>4</sub> is chosen from hydrogen, hydroxyl groups, methoxy groups, and C<sub>1</sub>-C<sub>4</sub> alkyl groups;

with the proviso that:

- (a) when R<sub>3</sub> is an amino group, then it occupies position 4;
- (b) when R<sub>3</sub> occupies position 4, then R<sub>4</sub> occupies position 7; and
- (c) when R<sub>3</sub> occupies position 5, then R<sub>4</sub> occupies position 6.

46. The composition according to Claim 44, wherein said benzimidazole derivatives are chosen from 4-hydroxybenzimidazole, 4-amino-benzimidazole, 4-hydroxy-7-methylbenzimidazole, 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-benzimidazole, 4-amino-2-methylbenzimidazole, 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-benzimidazole, 4,7-dihydroxybenzimidazole, 4,7-dihydroxy-1-methylbenzimidazole, 4,7-dimethoxy-benzimidazole, 5,6-dihydroxy-1-methylbenzimidazole, 5,6-dihydroxy-2-methylbenzimidazole, 5,6-dimethoxy-benzimidazole, and acid addition salts of said benzimidazole derivatives .

47. The composition according to Claim 44, wherein said benzimidazole derivatives are chosen from compounds of formula (II), and their acid addition salts:



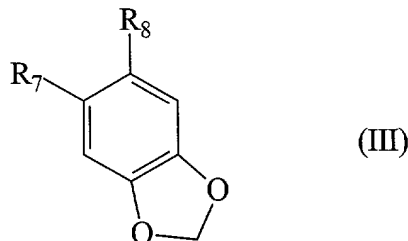
in which:

$R_5$  and  $R_6$ , which may be identical or different, are each chosen from hydrogen and  $C_1$ - $C_4$  alkyl groups; and

$Z$  is chosen from hydroxyl groups and amino groups.

48. The composition according to Claim 44, wherein said benzomorpholine derivatives are chosen from 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine, 6-amino-1,4-benzomorpholine, and acid addition salts of said benzomorpholine derivatives.

49. The composition according to Claim 44, wherein said sesamol derivatives are chosen from the compounds of formula (III) and their acid addition salts:



in which:

$R_7$  is chosen from hydroxyl groups, amino groups,  $(C_1$ - $C_4$ )alkylamino groups, monohydroxy  $(C_1$ - $C_4$ )alkylamino groups, and polyhydroxy $(C_2$ - $C_4$ )alkyl-amino groups;

$R_8$  is chosen from hydrogen, halogens, and  $(C_1$ - $C_4$ ) alkoxy groups.

50. The composition according to Claim 49, wherein said sesamol derivatives of formula III are chosen from 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-4,5-methylene-dioxyaniline and 2-( $\beta$ -hydroxy-ethyl)amino-4,5-methylene-dioxybenzene, and acid addition salts of said sesamol derivatives.

51. The composition according to Claim 44, wherein said pyrazoloazole derivatives are chosen from:

- 2-methylpyrazolo-1,2,4-triazole,
- 2-ethylpyrazolo-1,2,4-triazole,
- 2-isopropylpyrazolo-1,2,4-triazole,
- 2-phenylpyrazolo-1,2,4-triazole,
- 2,6-dimethylpyrazolo-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo-1,2,4-triazole,
- 3,6-dimethylpyrazolo-1,2,4-triazole,
- 6-phenyl-3-methylthiopyrazolo-1,2,4-triazole,
- 6-aminopyrazolo benzimidazole,

and acid addition salts of said pyrazoloazole derivatives.

52. The composition according to Claim 44, wherein said pyrroloazole derivatives are chosen from:

- 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo-1,2,4-triazole,
- 5-cyano-8-methyl-4-phenylpyrrolo-1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo benzimidazole,

and acid addition salts of said pyrroloazole derivatives.

53. The composition according to Claim 44, wherein said imidazoloazole derivatives are chosen from:

- 7,8-dicyanoimidazolo imidazole,
  - 7,8-dicyano-4-methylimidazolo imidazole,
- and acid addition salts of said imidazoloazole derivatives.

54. The composition according to Claim 44, wherein said pyrazolopyrimidine derivatives are chosen from:

- pyrazolo pyrimidin-7-one,
  - 2,5-dimethylpyrazolo pyrimidin-7-one,
  - 2-methyl-6-ethoxycarbonylpyrazolo pyrimidin-7-one,
  - 2-methyl-5-methoxymethylpyrazolo pyrimidin-7-one,
  - 2-tert-butyl-5-trifluoromethylpyrazolo pyrimidin-7-one,
  - 2,7-dimethylpyrazolo pyrimidin-5-one,
- and acid addition salts of said pyrazolopyrimidine derivatives.

55. The composition according to Claim 44, wherein said pyrazoline-3,5-dione derivatives are chosen from:

- 1,2-diphenylpyrazoline-3,5-dione,
  - 1,2-diethylpyrazoline-3,5-dione,
- and acid addition salts of said pyrazoline-3,5-dione derivatives.

56. The composition according to claim 32, wherein said at least one oxidation dye is present in a concentration ranging from about 0.0001% to about 12% by weight relative to the total weight of said composition.

57. The composition according to Claim 32, wherein said at least one oxidation dye is present in a concentration ranging from about 0.005% to about 6% by weight of the total weight of said composition.

58. The composition according to claim 32, further comprising:

(a) at least one benzenic oxidation base chosen from para-phenylenediamines, bis(phenylalkylenediamines, orthophenylenediamines, para-aminophenols, ortho-aminophenols, and acid addition salts of said benzenic oxidation base,

(b) at least one benzenic coupler chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols and acid addition salts of said benzenic coupler, and

(c) at least one direct dye.

59. The composition according to claim 32, wherein said acid addition salts of said at least one oxidation dye are chosen from hydrochlorides, hydrobromides, sulphates, tartrates, lactates, and acetates.

60. The composition according to claim 32, further comprising at least one carrier which is suitable for dyeing keratin fibers.

61. The composition according to claim 60, wherein said at least one carrier is chosen from water and at least one organic solvent.

62. The composition according to claim 32, wherein said composition has a pH ranging from about 4 to about 11.

63. A method of dyeing keratinous fibers, comprising the step of applying at least one dyeing composition to said keratinous fibers for a sufficient time to achieve a desired coloration, wherein said at least one dyeing composition comprises:

(a) at least one oxidation base chosen from heterocyclic oxidation bases, heterocyclic couplers, and acid addition salts of said oxidation dyes, provided that said heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy- pyrimidine and 3,4-diaminohydroxypyrazole; and provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds; and

(b) at least one enzyme of the laccase type.

64. A method for dyeing keratinous fibers comprising the steps of:

- (a) storing a first composition;
- (b) storing a second composition separately from said first composition;
- (c) mixing said first composition with said second composition to form a mixture; and
- (d) applying said mixture to said keratinous fibers for a sufficient time to achieve a desired coloration;

wherein said first composition comprises at least one oxidation base chosen from heterocyclic oxidation bases, heterocyclic couplers, and acid addition salts of said oxidation dyes, in a medium appropriate for dyeing keratinous fibers, provided that said

heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy- pyrimidine and 3,4-diaminohydroxypyrazole; and provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds; and

wherein said second composition comprises at least one enzyme of the laccase type, in a medium appropriate for dyeing keratinous fibers.

65. A multicompartment device or a dyeing kit, comprising:

a first compartment containing a first composition comprising at least one oxidation base chosen from heterocyclic oxidation bases, heterocyclic couplers, and acid addition salts of said oxidation dyes, provided that said heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy- pyrimidine and 3,4-diaminohydroxypyrazole; and provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds, in a medium appropriate for dyeing keratinous fibers; and

a second compartment containing a second composition comprising at least one enzyme of the laccase type, in a medium appropriate for dyeing keratinous fibers.--

#### REMARKS

Claims 1-31 have been canceled and new claims 32-65 are currently pending in this application. Support for claims 32-65 may be found in the specification as a whole, and claims 1-31, specifically. No new matter has been introduced by the amendments.

Amendment, please charge the fee to our Deposit Account No. 06-0916.

FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, L.L.P.

By: Cheryl Giljestrand  
Reg. No 45,275  
for Thomas L. Irving  
Reg. No. 28,619

LAW OFFICES  
FINNEGAN, HENDERSON,  
FARABOW, GARRETT,  
& DUNNER, L.L.P.  
1300 I STREET, N. W.  
WASHINGTON, DC 20005  
202-408-4000



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WO 99/36039

PCT/FR98/02831

1

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,  
CONTAINING A LACCASE, AND DYEING PROCESS USING THIS  
COMPOSITION

5           The invention relates to a composition for  
the oxidation dyeing of keratin fibres, and in  
particular of human keratin fibres such as the hair,  
comprising, in a medium which is suitable for dyeing,  
at least one heterocyclic oxidation dye and at least  
10 one laccase-type enzyme, as well as to the dyeing  
process using this composition.

It is known practice to dye keratin fibres,  
and in particular human hair, with dye compositions  
containing one or more oxidation dye precursors, in  
15 particular ortho- or para-phenylenediamines, ortho- or  
para-aminophenols, and heterocyclic bases, which are  
generally known as oxidation bases. These oxidation  
dyes (oxidation bases) are colourless or weakly  
coloured compounds which, when combined with oxidizing  
20 products, can give rise to coloured compounds and dyes  
by a process of oxidative condensation.

It is also known that the shades obtained  
with these oxidation bases can be varied by combining  
them with couplers or coloration modifiers, the latter  
25 being chosen in particular from aromatic meta-diamines,  
meta-aminophenols, meta-diphenols and certain  
heterocyclic compounds.

00500128.00300

The so-called "permanent" coloration obtained by means of these oxidation dyes should moreover satisfy a certain number of requirements. Thus, it should have no toxicological drawbacks, it should allow shades to be obtained in the desired intensity and it should have good staying power with respect to external agents (light, bad weather, washing, permanent-waving, perspiration or rubbing).

The oxidation dyeing of keratin fibres is generally carried out in alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide can have the drawback of resulting in substantial degradation of the fibres, as well as a decolorization of the keratin fibres, which is not always desirable.

25           The oxidation dyeing of keratin fibres can  
also be carried out using oxidizing systems other than  
hydrogen peroxide, such as enzymatic systems. Thus, it  
has already been proposed in US patent 3 251 742 and

patent applications FR-A-2 112 549, FR-A-2 694 018,  
EP-A-0 504 005, WO 95/07988, WO 95/33836, WO 95/33837,  
WO 96/00290, WO 97/19998 and WO 97/19999, to dye  
keratin fibres with compositions comprising at least  
5 one oxidation dye, or at least one melanin precursor,  
in combination with laccase-type enzymes, the said  
compositions being placed in contact with atmospheric  
oxygen. Although these dye formulations are used under  
conditions which do not result in the degradation of  
10 keratin fibres comparable to that generated by dyes  
used in the presence of hydrogen peroxide, they lead to  
colorations that are still insufficient both in terms  
of the homogeneity of the colour distributed along the  
fibre (unison) and in terms of the chromaticity  
15 (luminosity) and dyeing power.

The Applicant has now discovered that it is  
possible to obtain novel dyes that are capable of  
giving more intense colorations without generating any  
significant degradation of keratin fibres, and that are  
20 relatively unselective and stand up well to the various  
attacking factors to which the fibres may be subjected,  
by combining at least one suitably selected  
heterocyclic oxidation dye (oxidation base and/or  
coupler) and at least one laccase-type enzyme.

25 This discovery forms the basis of the present  
invention.

A first subject of the invention is thus a  
ready-to-use composition for the oxidation dyeing of

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keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing, - at least one oxidation dye chosen from heterocyclic oxidation bases and heterocyclic couplers, and - at least one laccase-type enzyme, the said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds and free of heterocyclic oxidation base chosen from 4,5-diamino-6-hydroxypyrimidine and 3,4-diaminohydroxypyrazole.

The ready-to-use dye composition in accordance with the invention leads to intense, chromatic colorations. The colorations obtained with the ready-to-use dye composition in accordance with the invention moreover show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather and with respect to perspiration and the various treatments to which hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this ready-to-use dye composition.

The laccase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from laccases of plant origin, of animal origin, of fungal origin (yeasts, moulds or

funghi) or of bacterial origin, it being possible for the organisms of origin to be monocellular or multicellular. The laccase(s) used in the ready-to-use dye composition in accordance with the invention can  
5 also be obtained by biotechnology.

Among the laccases of plant origin which can be used according to the invention, mention may be made of the laccases produced by plants which carry out chlorophyll synthesis, such as those mentioned in  
10 patent application FR-A-2 694 018.

Mention may be made in particular of the laccases present in extracts of Anacardiaceae plants such as, for example, extracts of *Magnifera indica*, of *Schinus molle* or of *Pleiogynium timoriense*; in extracts  
15 of Podocarpaceae plants, of *Rosmarinus* off., of *Solanum tuberosum*, of *Iris* sp., of *Coffea* sp., of *Daucus carota*, of *Vinca minor*, of *Persea americana*, of *Catharanthus roseus*, of *Musa* sp., of *Malus pumila*, of *Gingko biloba*, of *Monotropa hypopithys* (Indian pipe),  
20 of *Aesculus* sp., of *Acer pseudoplatanus*, of *Prunus persica* and of *Pistacia palaestina*.

Among the laccases of fungal origin, optionally obtained by biotechnology, which can be used according to the invention, mention may be made of the  
25 laccase(s) obtained from *Polyporus versicolor*, from *Rhizoctonia praticola* and from *Rhus vernicifera* as described, for example, in patent applications FR-A-2 112 549 and EP-A-504 005; the laccases described in

patent applications WO 95/07988, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, the content of which forms an integral part of the present description, such as, for example, the laccase(s)

- 5 obtained from *Scytalidium*, from *Polyporus pinsitus*, from *Myceliophthora thermophila*, from *Rhizoctonia solani*, from *Pyricularia oryzae*, and variants thereof. Mention may also be made of the laccase(s) obtained from *Trametes versicolor*, from *Fomes fomentarius*, from
- 10 *Chaetomium thermophile*, from *Neurospora crassa*, from *Colorius versicolor*, from *Botrytis cinerea*, from *Rigidoporus lignosus*, from *Phellinus noxius*, from *Pleurotus ostreatus*, from *Aspergillus nidulans*, from *Podospora anserina*, from *Agaricus bisporus*, from
- 15 *Ganoderma lucidum*, from *Glomerella cingulata*, from *Lactarius piperatus*, from *Russula delica*, from *Heterobasidion annosum*, from *Thelephora terrestris*, from *Cladosporium cladosporioides*, from *Cerrena unicolor*, from *Coriolus hirsutus*, from *Ceriporiopsis*
- 20 *subvermispora*, from *Coprinus cinereus*, from *Panaeolus papilionaceus*, from *Panaeolus sphinctrinus*, from *Schizophyllum commune*, from *Dichomitius squalens*, and from variants thereof.

- Laccases of fungal origin, optionally
- 25 obtained by biotechnology, will more preferably be chosen.

The enzymatic activity of the laccases used in accordance with the invention and having

5 syringaldazine per minute at a pH of 5.5 and at a temperature of 30°C. One U unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 530 nm, using syringaldazine as substrate, at 30°C and at a pH of 6.5.

10 The enzymatic activity of the laccases used according to the invention can also be defined by the oxidation of para-phenylenediamine. One ulac unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 496.5 nm, using  
15 para-phenylenediamine as substrate (64 mM), at 30°C and at a pH of 5.

According to the invention, the enzymatic activity is preferably determined in ulac units.

Among the heterocyclic oxidation bases which  
20 can be used in the ready-to-use dye composition  
according to the invention, mention may be made in  
particular of pyrimidine derivatives and pyrazole  
derivatives, and the addition salts thereof with an  
acid.

25            Among the pyrimidine derivatives which may be  
mentioned more particularly are the compounds  
described, for example, in German patent DE 2 359 399  
or Japanese patents JP 88-169 571 and JP 91-333 495,

such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, and the addition salts thereof with an acid and pyrazolo-pyrimidine derivatives such as pyrazolo[1,5-a]pyrimidine-3,7-diamine,

5 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, pyrazolo[1,5-a]pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine, 3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-

10 methylpyrazolo[1,5-a]pyrimidin-7-ol, 3-aminopyrazolo[1,5-a]pyrimidin-5-ol, 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 3-amino-7- $\beta$ -hydroxyethylamino-5-methylpyrazolo-[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-

15 3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-amino-pyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]-ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-

20 3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo-[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives which may be

25 mentioned more particularly are the compounds described in patents or patent applications DE 3 843 892, DE 4 133 957, DE 4 234 886, WO 94/08969, WO 94/08970, DE 4 234 887, FR 2 733 749, FR 2 735 685, such as

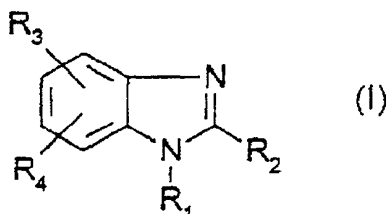


4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole,  
 1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole,  
 1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-  
 dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-  
 5 phenylpyrazole, 4,5-diamino-1-tert-butyl-3-  
 methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-  
 pyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole,  
 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,  
 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,  
 10 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,  
 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and  
 4,5-diamino-3-methyl-1-isopropylpyrazole, and the  
 addition salts thereof with an acid.

Among the heterocyclic couplers which can be  
 15 used in the ready-to-use dye composition in accordance  
 with the invention, mention may be made in particular  
 of benzimidazole derivatives, benzomorpholine  
 derivatives, sesamol derivatives, pyrazoloazole  
 derivatives, pyrroloazole derivatives, imidazoloazole  
 20 derivatives, pyrazolopyrimidine derivatives,  
 pyrazoline-3,5-dione derivatives, pyrrolo-  
 [3,2-d]oxazoline derivatives, pyrazolo[3,4-d]thiazole  
 derivatives, thiazoloazole S-oxide derivatives and  
 thiazoloazole S,S-dioxide derivatives, and the addition  
 25 salts thereof with an acid.

Among the benzimidazole derivatives which can  
 be used as heterocyclic couplers in the dye composition  
 in accordance with the invention, mention may be made

more particularly of the compounds of formula (I)  
below, and the addition salts thereof with an acid:



in which:

- 5  $R_1$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl radical,  
 $R_2$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl or phenyl  
 radical,  
 $R_3$  represents a hydroxyl, amino or methoxy radical,  
 $R_4$  represents a hydrogen atom or a hydroxyl, methoxy or  
 10  $C_1$ - $C_4$  alkyl radical;  
 with the proviso that:
- when  $R_3$  denotes an amino radical, then it occupies  
 position 4,
  - when  $R_3$  occupies position 4, then  $R_4$  occupies position  
 15 7,
  - when  $R_3$  occupies position 5, then  $R_4$  occupies position  
 6.

Among the benzimidazole derivatives of  
 formula (I) above which may be mentioned more  
 20 particularly are 4-hydroxybenzimidazole,  
 4-aminobenzimidazole, 4-hydroxy-7-methylbenzimidazole,  
 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-  
 benzimidazole, 4-amino-2-methylbenzimidazole,  
 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-

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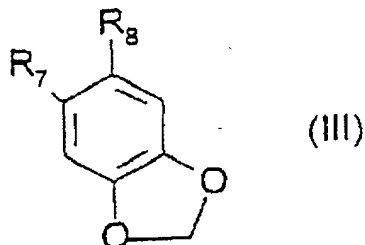


in which:

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Among the sesamol derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition, mention may be made more particularly of the compounds of formula (III) below, and the addition  
5 salts thereof with an acid:



in which:

- R<sub>7</sub> denotes a hydroxyl, amino, (C<sub>1</sub>-C<sub>4</sub>)alkylamino, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino or polyhydroxy(C<sub>2</sub>-C<sub>4</sub>)alkyl-  
10 amino radical,
- R<sub>8</sub> denotes a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkoxy radical.

Among the sesamol derivatives of formula (III) above which may be mentioned more particularly  
15 are 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-4,5-methylenedioxyaniline and 2-(β-hydroxyethyl)amino-4,5-methylenedioxybenzene, and the addition salts thereof with an acid.

Among the pyrazoloazole derivatives which can  
20 be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patents and patent applications: FR 2 075 583, EP-A-119 860, EP-A-285 274,

5 JP 85/172982, JP 85/190779 as well as in the following  
publications: Chem. Ber. 32, 797 (1899), Chem. Ber. 89,  
2550, (1956), J. Chem. Soc. Perkin trans 1, 2047,  
(1977), J. Prakt. Chem., 320, 533, (1978); the  
teachings of which form an integral part of the present  
10 patent application.

15 - 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,  
- 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,  
- 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,  
- 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,  
- 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,  
20 - 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,  
- 6-aminopyrazolo[1,5-a]benzimidazole,  
and the addition salts thereof with an acid.

Among the pyrroloazole derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent applications and patents: US 5 256 526, EP-A-557 851, EP-A-578 248,

EP-A-518 238, EP-A-456 226, EP-A-488 909, EP-A-488 248,  
and in the following publications:

- D.R. Liljegren Ber. 1964, 3436;
- E.J. Browne, J.C.S., 1962, 5149;
- 5 - P. Magnus, J.A.C.S., 1990, 112, 2465;
- P. Magnus, J.A.C.S., 1987, 109, 2711;
- Angew. Chem. 1960, 72, 956;
- and Rec. Trav. Chim. 1961, 80, 1075; the teachings of  
which form an integral part of the present patent  
10 application.

Pyrroloazole derivatives which may be  
mentioned most particularly are:

- 5-cyano-4-ethoxycarbonyl-8-méthylpyrrolo[1,2-b]-  
1,2,4-triazole,
- 15 - 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-  
1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole,  
and the addition salts thereof with an acid.

Among the imidazoloazole derivatives which  
20 can be used as heterocyclic couplers in the ready-to-  
use dye composition in accordance with the invention,  
mention may be made more particularly of the compounds  
described in the following patent applications and  
patents: US 5 441 863; JP 62-279 337; JP 06-236 011 and  
25 JP 07-092 632, the teachings of which form an integral  
part of the present patent application.

Imidazoloazole derivatives which may be  
mentioned most particularly are:

- 7,8-dicyanoimidazolo[3,2-a]imidazole,
  - 7,8-dicyano-4-methylimidazolo[3,2-a]imidazole,
- and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives

5 which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent application: EP-A-304 001, the teaching of which forms

10 an integral part of the present patent application.

Pyrazolopyrimidine derivatives which may be mentioned most particularly are:

- pyrazolo[1,5-a]pyrimidin-7-one,
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
- 15 - 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-
- 20 a]pyrimidin-7-one,
- 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the addition salts thereof with an acid.

Among the pyrazoline-3,5-dione derivatives which can be used as heterocyclic couplers in the

25 ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent

applications and patents: JP 07-036159, JP 07-084348  
and US 4 128 425, and in the following publications:

- L. WYZGOWSKA, Acta. Pol. Pharm. 1982, 39 (1-3), 83.
  - E. HANNIG, Pharmazie, 1980, 35 (4), 231
  - 5 - M.H. ELNAGDI, Bull. Chem. Soc. Jap., 46 (6), 1830,  
1973
  - G. CARDILLO, Gazz. Chim. Ital. 1966, 96, (8-9), 973,
- the teachings of which form an integral part of the  
present patent application.

10               Pyrazoline-3,5-dione derivatives which may be  
mentioned most particularly are:

- 1,2-diphenylpyrazoline-3,5-dione,
  - 1,2-diethylpyrazoline-3,5-dione,
- and the addition salts thereof with an acid.

15               Among the pyrrolo[3,2-d]oxazole derivatives  
which can be used as heterocyclic couplers in the  
ready-to-use dye composition in accordance with the  
invention, mention may be made more particularly of the  
compounds described in patent application

20 JP 07 325 375, the teaching of which forms an integral  
part of the present patent application.

              Among the pyrazolo[3,4-d]thiazole derivatives  
which can be used as heterocyclic couplers in the  
ready-to-use dye composition in accordance with the  
25 invention, mention may be made more particularly of  
compounds described in patent application JP 07 244 361  
and in J. Heterocycl. Chem. 16, 13, (1979).



Among the thiazoloazole S-oxide and thiazoloazole S,S-dioxide derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention  
5 may be made more particularly of the compounds described in the following documents:

- JP 07 09 84 89;
- Khim. Geterotsilk. Soedin, 1967, p. 93;
- J. Prakt. Chem., 318, 1976, p. 12;
- 10 - Indian J. Heterocycl. Chem. 1995, 5 (2), p. 135;
- Acta. Pol. Pharm. 1995, 52 (5), 415;
- Heterocycl. Commun. 1995, 1 (4), 297;
- Arch. Pharm. (Weinheim, Ger.), 1994, 327 (12), 825.

The heterocyclic oxidation dye(s), i.e. the  
15 heterocyclic oxidation base(s) and/or the heterocyclic coupler(s) preferably represent(s) from 0.0001% to 12% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005% to 6% by weight approximately  
20 relative to this weight.

The ready-to-use dye composition in accordance with the invention can also contain, in addition to the heterocyclic oxidation dyes defined above, at least one benzenic oxidation base and/or at  
25 least one benzenic coupler and/or at least one direct dye, in particular to modify the shades or to enrich them with glints.

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In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and

couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or support) for the ready-to-use dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble.

10           The pH of the ready-to-use composition in  
accordance with the invention is chosen such that the  
enzymatic activity of the laccase is sufficient. It is  
generally between 4 and 11 approximately, and  
preferably between 6 and 9 approximately. It can be  
15 adjusted to the desired value by means of acidifying or  
basifying agents usually used in the dyeing of keratin  
fibres.

The ready-to-use dye composition in accordance with the invention can also contain various  
20 adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, polymers, antioxidants, enzymes other than the laccases used in accordance with the invention, such  
25 as, for example, peroxidases or 2-electron-oxidoreductases, penetrating agents, sequestering agents, fragrances, buffers, dispersants, film-forming

agents, preserving agents, opacifiers, thickeners and vitamins.

Needless to say, the person skilled in the art will take care to select this or these optionally  
5 additional compound(s) such that the advantageous properties intrinsically associated with the ready-to-use dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

10           The ready-to-use dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which may be pressurized, or in any other form which is suitable for dyeing keratin fibres, and in particular  
15 human hair. In this case, the heterocyclic oxidation dye(s) and optionally the additional oxidation dye(s) and the laccase-type enzyme(s) are present in the same ready-to-use composition, and consequently the said composition should be free of gaseous oxygen, so as to  
20 avoid any premature oxidation of the oxidation dye(s).

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.

25                   According to this process, at least one  
ready-to-use dye composition as defined above is  
applied to the fibres for a period which is sufficient  
to develop the desired coloration, after which the

fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is generally between 3 minutes and 60 minutes and even more specifically between 5 minutes and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step consisting in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation dye chosen from the heterocyclic oxidation bases and heterocyclic couplers as defined above, and, on the other hand, a composition (B) comprising, in a medium which is suitable for dyeing, at least one laccase-type enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices may be equipped with means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

The example which follows is intended to illustrate the invention without thereby limiting its scope.

DYEING EXAMPLE

- 5                   The following ready-to-use dye compositions were prepared (contents in grams):

COMPOSITION	1	2
2,4,5,6-Tetraaminopyrimidine sulphate (heterocyclic oxidation base)	0.65	-
para-Phenylenediamine (benzenic oxidation base)	-	0.20
Resorcinol (benzenic coupler)	0.30	-
2-Methoxy-4,5-methylenedioxyaniline monohydrochloride (heterocyclic coupler)	-	0.37
Laccase obtained from Rhus vernicifera at 180 units/mg, sold by the company Sigma	1.8	1.8
Common dye support (*)	(*)	(*)
Demineralized water qs	100 g	100 g

(\*): Common dye support:

- Ethanol 20.0 g
- 10 - (C8-C10)alkylpolyglucoside as an  
aqueous solution containing 60%  
active material (A.M.), sold under  
the name Oramix CG110® by the  
company Seppic 4.8 g A.M.
- 15 - Agent for pH q.s. pH = 6.5

Each of the ready-to-use dye compositions described above was applied to locks of natural grey hair containing 90% white hairs, for 40 minutes at a temperature of 30°C. The hair was then rinsed, washed  
5 with a standard shampoo and then dried.

The hair was dyed in the shades given in the Table below:

EXAMPLE	Shade obtained
1	Coppery mahogany light blond
2	light blond

In the dye compositions described above, the  
10 laccase from *Rhus vernicifera* at 180 units/mg, sold by the company Sigma, can be replaced with 1.0 g of laccase from *Pyricularia oryzae* at 100 units/mg, sold by the company ICN.

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## CLAIMS

1. Ready-to-use composition for the oxidation dyeing of keratin fibres, and in particular  
5 of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing,  
- at least one oxidation dye chosen from heterocyclic oxidation bases and heterocyclic couplers, and  
10 - at least one laccase-type enzyme,  
the said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds and free of heterocyclic oxidation  
base chosen from 4,5-diamino-6-hydroxypyrimidine and  
15 3,4-diaminohydroxypyrazole.
2. Composition according to Claim 1, characterized in that the laccase is chosen from laccases of plant origin, of animal origin, of fungal origin or of bacterial origin and from laccases  
20 obtained by biotechnology.
3. Composition according to either of Claims 1 and 2, characterized in that the laccase is of plant origin and chosen from the laccases present in  
extracts of Anacardiaceae plants, of Podocarpaceae  
25 plants, of Rosmarinus off., of Solanum tuberosum, of Iris sp., of Coffea sp., of Daucus carota, of Vinca minor, of Persea americana, of Catharanthus roseus, of



Musa sp., of Malus pumila, of Ginkgo biloba, of  
Monotropa hypopithys (Indian pipe), of Aesculus sp., of  
Acer pseudoplatanus, of Prunus persica and of Pistacia  
palaestina.

5                    4.      Composition according to Claim 1 or 2,  
characterized in that the laccase is of microbial  
origin or obtained by biotechnology.

5. Composition according to Claim 4, characterized in that the laccase is chosen from laccases obtained from *Polyporus versicolor*, from *Rhizoctonia praticola*, from *Rhus vernicifera*, from *Scytalidium*, from *Polyporus pinsitus*, from *Myceliophthora thermophila*, from *Rhizoctonia solani*, from *Pyricularia oryzae*, from *Trametes versicolor*, from *Fomes fomentarius*, from *Chaetomium thermophile*, from *Neurospora crassa*, from *Colorius versicolor*, from *Botrytis cinerea*, from *Rigidoporus lignosus*, from *Phellinus noxius*, from *Pleurotus ostreatus*, from *Aspergillus nidulans*, from *Podospora anserina*, from *Agaricus bisporus*, from *Ganoderma lucidum*, from *Glomerella cingulata*, from *Lactarius piperatus*, from *Russula delica*, from *Heterobasidion annosum*, from *Thelephora terrestris*, from *Cladosporium cladosporioides*, from *Cerrena unicolor*, from *Coriolus hirsutus*, from *Ceriporiopsis subvermispora*, from *Coprinus cinereus*, from *Panaeolus papilionaceus*, from *Panaeolus sphinctrinus*, from *Schizophyllum commune* and from *Dichomitius squalens*, and from variants thereof.

6. Composition according to any one of the preceding claims, characterized in that the amount of laccase(s) is between 0.5 Lacu and 200 Lacu per 100 g of dye composition.

5 7. Composition according to any one of the preceding claims, characterized in that the heterocyclic oxidation base(s) is(are) chosen from pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

10 8. Composition according to Claim 7, characterized in that the pyrimidine derivatives are chosen from 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine and pyrazolopyrimidine derivatives, and the addition salts thereof with an  
15 acid.

9. Composition according to Claim 8, characterized in that the pyrazolopyrimidine derivatives are chosen from pyrazolo[1,5-a]pyrimidine-3,7-diamine, 2-methylpyrazolo[1,5-a]pyrimidine-  
20 3,7-diamine, 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, pyrazolo[1,5-a]pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine, 3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-methylpyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-  
25 pyrazolo[1,5-a]pyrimidin-5-ol, 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 3-amino-7- $\beta$ -hydroxyethylamino-5-methylpyrazolo[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol,

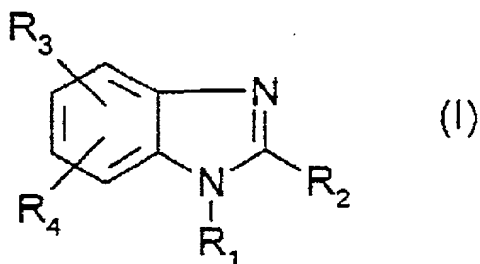
2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 5 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

10 10. Composition according to Claim 7, characterized in that the pyrazole derivatives are chosen from 4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole, 1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 15 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 20 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and 4,5-diamino-3-methyl-1-isopropylpyrazole, and the addition salts thereof with an acid.

25 11. Composition according to any one of the preceding claims, characterized in that the heterocyclic coupler(s) is(are) chosen from benzimidazole derivatives, benzomorpholine derivatives,

sesamol derivatives, pyrazoloazole derivatives,  
 pyrroloazole derivatives, imidazoloazole derivatives,  
 pyrazolopyrimidine derivatives, pyrazoline-3,5-dione  
 derivatives, pyrrolo[3,2-d]oxazoline derivatives,  
 5 pyrazolo[3,4-d]thiazole derivatives, thiazoloazole S-  
 oxide derivatives and thiazoloazole S,S-dioxide  
 derivatives, and the addition salts thereof with an  
 acid.

12. Composition according to Claim 11,  
 10 characterized in that the benzimidazole derivatives are  
 chosen from the compounds of formula (I) below, and the  
 addition salts thereof with an acid:



in which:

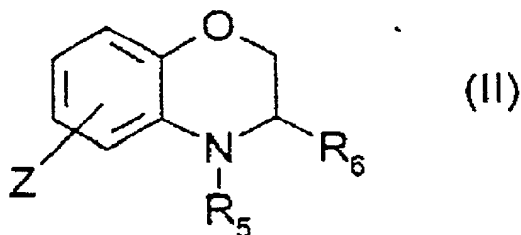
- 15  $R_1$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl radical,  
 $R_2$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl or phenyl  
 radical,  
 $R_3$  represents a hydroxyl, amino or methoxy radical,  
 $R_4$  represents a hydrogen atom or a hydroxyl, methoxy or  
 20  $C_1$ - $C_4$  alkyl radical;  
 with the proviso that:  
 - when  $R_3$  denotes an amino radical, then it occupies  
 position 4,

- when  $R_3$  occupies position 4, then  $R_4$  occupies position 7,

- when  $R_3$  occupies position 5, then  $R_4$  occupies position 6.

5            13. Composition according to Claim 12,  
characterized in that the benzimidazole derivatives are  
chosen from 4-hydroxybenzimidazole, 4-amino-  
benzimidazole, 4-hydroxy-7-methylbenzimidazole,  
4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-  
10 benzimidazole, 4-amino-2-methylbenzimidazole,  
5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-  
benzimidazole, 4,7-dihydroxybenzimidazole,  
4,7-dihydroxy-1-methylbenzimidazole, 4,7-dimethoxy-  
benzimidazole, 5,6-dihydroxy-1-methylbenzimidazole,  
15 5,6-dihydroxy-2-methylbenzimidazole and 5,6-dimethoxy-  
benzimidazole, and the addition salts thereof with an  
acid.

          14. Composition according to Claim 11,  
characterized in that the benzomorpholine derivatives  
20 are chosen from the compounds of formula (II) below,  
and the addition salts thereof with an acid:

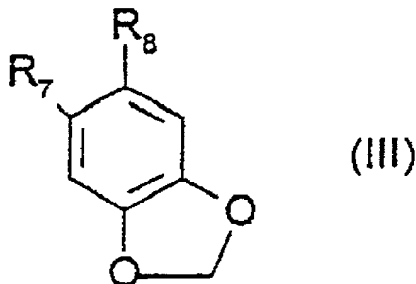


in which:

$R_5$  and  $R_6$ , which may be identical or different, represent a hydrogen atom or a  $C_1$ - $C_4$  alkyl radical,  $Z$  represents a hydroxyl or amino radical.

15. Composition according to Claim 14, characterized in that the benzomorpholine derivatives are chosen from 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine and 6-amino-1,4-benzomorpholine, and the addition salts thereof with an acid.

10 16. Composition according to Claim 11, characterized in that the sesamol derivatives are chosen from the compounds of formula (III) below, and the addition salts thereof with an acid:



15 in which:

-  $R_7$  denotes a hydroxyl, amino,  $(C_1$ - $C_4$ )alkylamino, monohydroxy $(C_1$ - $C_4$ )alkylamino or polyhydroxy $(C_2$ - $C_4$ )alkylamino radical,

-  $R_8$  denotes a hydrogen or halogen atom or a  $C_1$ - $C_4$  alkoxy radical.

20

17. Composition according to Claim 16, characterized in that the sesamol derivatives are chosen from 2-bromo-4,5-methylenedioxyphenol,

2-methoxy-4,5-methylenedioxyaniline and 2-( $\beta$ -hydroxy-ethyl)amino-4,5-methylenedioxybenzene, and the addition salts thereof with an acid.

18. Composition according to Claim 11,
- 5 characterized in that the pyrazoloazole derivatives are chosen from:
- 2-methylpyrazolo[1,5-b]-1,2,4-triazole,
  - 2-ethylpyrazolo[1,5-b]-1,2,4-triazole,
  - 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,
  - 10 - 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,
  - 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
  - 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
  - 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,
  - 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,
  - 15 - 6-aminopyrazolo[1,5-a]benzimidazole,
- and the addition salts thereof with an acid.

19. Composition according to Claim 11,
- characterized in that the pyrroloazole derivatives are chosen from:
- 20 - 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo[1,2-b]-1,2,4-triazole,
  - 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-1,2,4-triazole,
  - 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole,
  - 25 and the addition salts thereof with an acid.

20. Composition according to Claim 11,

characterized in that the imidazoloazole derivatives are chosen from:

- 7,8-dicyanoimidazolo[3,2-a]imidazole,
  - 7,8-dicyano-4-methylimidazolo[3,2-a]imidazole,
- and the addition salts thereof with an acid.

21. Composition according to Claim 11,
- 5 characterized in that the pyrazolopyrimidine derivatives are chosen from:
- pyrazolo[1,5-a]pyrimidin-7-one,
  - 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
  - 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-
  - 10 7-one,
  - 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-7-one,
  - 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-a]pyrimidin-7-one,
  - 15 - 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the addition salts thereof with an acid.

22. Composition according to Claim 11,
- characterized in that the pyrazoline-3,5-dione derivatives are chosen from:
- 20 - 1,2-diphenylpyrazoline-3,5-dione,
  - 1,2-diethylpyrazoline-3,5-dione,
- and the addition salts thereof with an acid.

23. Composition according to any one of the preceding claims, characterized in that the
- 25 heterocyclic oxidation dye(s) represent(s) from 0.0001% to 12% by weight relative to the total weight of the ready-to-use dye composition.



24. Composition according to Claim 23, characterized in that the heterocyclic oxidation dye(s) represent(s) from 0.005% to 6% by weight relative to the total weight of the ready-to-use dye composition.

5 25. Composition according to any one of the preceding claims, characterized in that it contains at least one benzenic oxidation base chosen from para-phenylenediamines, bis(phenylalkylenediamines, orthophenylenediamines, para-aminophenols and ortho-aminophenols, and the addition salts thereof with an acid, and/or at least one benzenic coupler chosen from meta-phenylenediamines, meta-aminophenols and meta-diphenols and the addition salts thereof with an acid, and/or at least one direct dye.

15 26. Composition according to any one of the preceding claims, characterized in that the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

20 27. Composition according to any one of the preceding claims, characterized in that the medium which is suitable for dyeing consists of water or of a mixture of water and at least one organic solvent.

25 28. Composition according to any one of the preceding claims, characterized in that it has a pH of between 4 and 11.

29. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair,

characterized in that at least one ready-to-use dye composition as defined in any one of the preceding claims is applied to the said fibres, for a period which is sufficient to develop the desired coloration.

- 5           30. Process according to Claim 29, characterized in that it includes a preliminary step which consists in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one heterocyclic
- 10 oxidation dye as defined in any one of Claims 1, 7 to 24 and 26, and, on the other hand, a composition (B) comprising in a medium which is suitable for dyeing, at least one laccase-type enzyme, and then in mixing them
- 15 together at the time of use, after which this mixture is applied to the keratin fibres.

31. Multi-compartment dyeing device or "kit", characterized in that it includes a first compartment comprising composition (A) as defined in Claim 30 and a second compartment comprising
- 20 composition (B) as defined in Claim 30.

# Declaration and Power of Attorney for Patent Application

## Déclaration et Pouvoir pour Demand de Brevet

### French Language Declaration

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que:

As a below named inventor, I hereby declare that:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

My residence, post office address and citizenship are as stated next to my name.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

KERATINOUS FIBRE OXIDATION DYEING  
COMPOSITION CONTAINING A LACCASE AND  
DYEING METHOD USING SAME

et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée:

the specification of which is attached hereto unless the following box is checked:

☒ a été déposée le \_\_\_\_\_  
sous le numéro de demande des Etats-Unis ou le  
numéro de demande international PCT  
\_\_\_\_\_ et modifiée  
\_\_\_\_\_ (les cas échéant).

☒ was filed on December 22, 1998 as United States  
Application Number or PCT International  
Application Number PCT/FR98/02831 and was  
amended on \_\_\_\_\_ (if applicable).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

**French Language Declaration**

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior foreign application(s)  
Demande(s) de brevet antérieure(s)

98/00,258 France  
(Number) (Country)  
(Numéro) (Pays)

(Number) (Country)  
(Numéro) (Pays)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

(Application No.) (Filing Date)  
(N° de demande) (Date de dépôt)

(Application No.) (Filing Date)  
(N° de demande) (Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont laquelle est devenue disponible entre la date de dépôt de la demande antérieure, et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

(Application No.) (Filing Date)  
(N° de demande) (Date de dépôt)

(Application No.) (Filing Date)  
(N° de demande) (Date de dépôt)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International Application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed  
Droit de priorité non revendiqué

13 January 1998  
(Day/Month/Year Filed)  
(Jour/Mois/Année de dépôt)

☐

(Day/Month/Year Filed)  
(Jour/Mois/Année de dépôt)

☐

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International Application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose any or all information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Status) (patented, pending, abandoned)  
(Status) (breveté, en cours d'examen, abandonné)

(Status) (patented, pending, abandoned)  
(Status) (breveté, en cours d'examen, abandonné)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**French Language Declaration**

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec L'Office des brevets et des marques: *(mentionner le nom et le numéro d'enregistrement)*.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this patent application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number)*:

**FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.**, Reg. No. 22,540; Douglas B. Henderson, Reg. No. 20,291; Ford F. Farabow, Jr., Reg. No. 20,630; Arthur S. Garrett, Reg. No. 20,338; Donald R. Dunner, Reg. No. 19,073; Brian G. Brunsvold, Reg. No. 22,593; Tipton D. Jennings, IV, Reg. No. 20,645; Jerry D. Voight, Reg. No. 23,020; Laurence R. Heffer, Reg. No. 20,827; Kenneth E. Payne, Reg. No. 23,098; Herbert H. Mintz, Reg. No. 26,691; C. Larry O'Rourke, Reg. No. 26,014; Albert J. Santorelli, Reg. No. 22,610; Michael C. Elmer, Reg. No. 25,857; Richard H. Smith, Reg. No. 20,609; Stephen L. Peterson, Reg. No. 26,325; John M. Romary, Reg. No. 26,331; Bruce C. Zotter, Reg. No. 27,680; Dennis P. O'Reilly, Reg. No. 27,932; Allen M. Sokal, Reg. No. 26,695; Robert D. Bajefsky, Reg. No. 25,387; Richard L. Stroup, Reg. No. 28,478; David W. Hill, Reg. No. 28,220; Thomas L. Irving, Reg. No. 28,619; Charles E. Lipsey, Reg. No. 28,165; Thomas W. Winland, Reg. No. 27,605; Basil J. Lewris, Reg. No. 28,818; Martin I. Fuchs, Reg. No. 28,508; E. Robert Yoches, Reg. No. 30,120; Barry W. Graham, Reg. No. 29,924; Susan Haberman Griffen, Reg. No. 30,907; Richard B. Racine, Reg. No. 30,415; Thomas H. Jenkins, Reg. No. 30,857; Robert E. Converse, Jr., Reg. No. 27,432; Clair X. Mullen, Jr., Reg. No. 20,348; Christopher P. Foley, Reg. No. 31,354; John C. Paul, Reg. No. 30,413; Roger D. Taylor, Reg. No. 28,992; David M. Kelly, Reg. No. 30,953; Kenneth J. Meyers, Reg. No. 25,146; Carol P. Einaudi, Reg. No. 32,220; Walter Y. Boyd, Jr., Reg. No. 31,738; Steven M. Anzalone, Reg. No. 32,095; Jean B. Fordis, Reg. No. 32,984; Barbara C. McCurdy, Reg. No. 32,120; James K. Hammond, Reg. No. 31,964; Richard V. Burgujian, Reg. No. 31,744; J. Michael Jakes, Reg. No. 32,824; Dirk D. Thomas, Reg. No. 32,600; Thomas W. Banks, Reg. No. 32,719; Christopher P. Isaac, Reg. No. 32,616; Bryan C. Diner, Reg. No. 32,409; M. Paul Barker, Reg. No. 32,013; Andrew Chanhon Sonu, Reg. No. 33,457; David S. Forman, Reg. No. 33,694; Vincent P. Kovalick, Reg. No. 32,867; James W. Edmondson, Reg. No. 33,871; Michael R. McGurk, Reg. No. 32,045; Joann M. Neth, Reg. No. 36,363; Gerson S. Panitch, Reg. No. 33,751; Cheri M. Taylor, Reg. No. 33,216; Charles E. Van Horn, Reg. No. 40,266; Linda A. Wadler, Reg. No. 33,218; Jeffrey A. Berkowitz, Reg. No. 36,743; Michael R. Kelly, Reg. No. 33,921; and James B. Monroe, Reg. No. 33,971; and Thalia V. Warnement, Reg. No. 39,064; Michele C. Bosch, Reg. No. 40,524; Allen R. Jensen, Reg. No. 28,224; Mark D. Sweet, Reg. No. 41,469; and Anthony M. Gutowski, Reg. No. 38,742.

Addresser toute correspondance à:

Send all Correspondence to:

**FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.**  
1300 I Street, N.W., Washington, D.C. 20005,  
Telephone No. (202) 408-4000.

Addresser tout appel téléphonique à:  
*(nom et numéro de téléphone)*

Direct all Telephone Calls to:  
*(name and telephone number)*

Thomas L. Irving, Reg. No. 28,619  
Telephone Number (202) 408-4082

Nom complet de l'unique ou premier inventeur: 1-0		Full name of sole or first inventor Gérard LANG	
Signature de l'inventeur	Date	Inventor's signature Gérard Lang	Date 08/21/2000
Domicile		Residence 51B, rue Robert Thomas, F-95390 Saint Prix, France FR	
Nationalité:		Citizenship French	
Adresse postale:		Post Office Address Same as residence	
Nom complet du second co-inventeur, le cas échéant: 2-0		Full name of second joint inventor, if any: Jean COTTERET	
Signature du second inventeur	Date	Second Inventor's signature Jean COTTERET	Date 08/21/2000
Domicile:		Residence 13, rue du Pré Rousselin, F-78480 Verneuil sur Seine, France	
Nationalité:		Citizenship French FR	
Adresse postale:		Post Office Address Same as residence	
Nom complet du third co-inventeur, le cas échéant:		Full name of third joint inventor, if any:	
Signature d'inventeur	Date	Third Inventor's signature	Date
Domicile		Residence	
Nationalité:		Citizenship	
Adresse postale:		Post Office Address	